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4-Chlorobenzoic acid *N,N*-dimethylformamide solvate

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Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.002 Å
R factor = 0.035
wR factor = 0.086
Data-to-parameter ratio = 17.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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In the title compound, $C_7H_5ClO_2.C_3H_7NO$, the carboxylic acid group of 4-chlorobenzoic acid is hydrogen bonded to a molecule of *N,N*-dimethylformamide *via* an $R_2^2(7)$ O—H···O/C—H···O motif. This motif takes precedence over the $R_2^2(8)$ O—H···O dimer arrangement observed in 4-chlorobenzoic acid itself.

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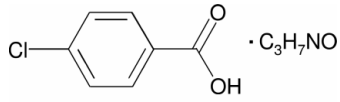
Comment

4-Chlorobenzoic acid (CBA) crystallizes as hydrogen-bonded $R_2^2(8)$ O—H···O dimers and dynamic proton transfer within the hydrogen bonds mediates the interconversion of two inequivalent dimeric forms (Horsewill *et al.*, 2003; Wilson *et al.*, 2004).



(I)

The title compound, (I), was crystallized to determine whether the $R_2^2(8)$ motif, and the proton-transfer process, is preserved in the solvate (Fig. 1). Significant deviations from idealized aromatic geometry in the CBA molecule of (I) include a marked widening of the internal ring angle at C4 [122.26 (12)°] and a concomitant narrowing of the angles *ortho* to this at C3 [118.25 (12)°] and C5 [118.81 (13)°]. Utilizing the angular substituent parameters for Cl and COOH (Domenicano, 1992), the corresponding predicted internal ring angles of 122.1 (C4) and 118.7° (C3 and C5) are in good agreement with the observed values. Thus, it may be concluded that the distortions from ideal sp^2 ring geometry are in line with expectations based on Domenicano's assessment of structural substituent effects in benzene derivatives. The $R_2^2(8)$ motif in CBA [Fig. 2, top, determined from single-crystal neutron diffraction data at 100 K (Wilson *et al.*, 2004)] is not preserved in (I). Instead, one CBA molecule is replaced by one molecule of *N,N*-dimethylformamide (DMF), forming an $R_2{}^2(7)$ O—H···O/C—H···O motif (Fig. 2, bottom), eliminating the possibility of a concerted two-proton transfer process. This interaction with DMF is not unexpected, as the $R_2^2(7)$ motif has been observed to recur with a reasonable frequency in the DMF solvates of carboxylic acids (Dale & Elsegood, 2004).

Experimental

A single-crystal sample of the title compound was recrystallized from DMF solution by slow evaporation at room temperature.

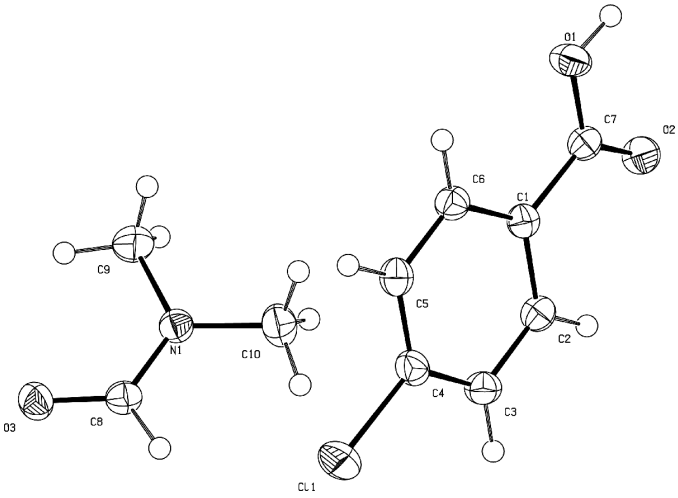


Figure 1
The molecular structure of (I), shown with 50% probability displacement ellipsoids.

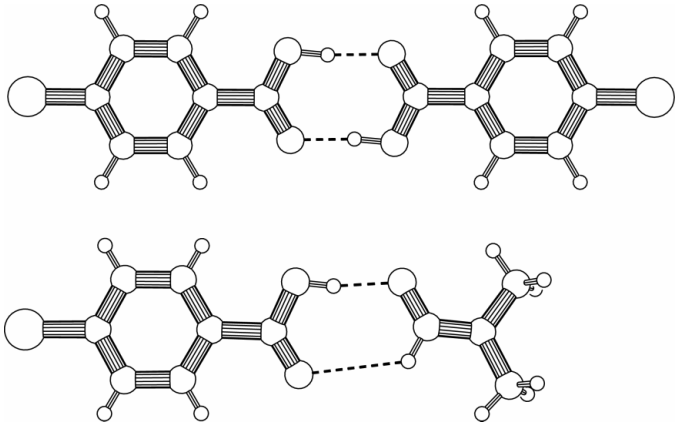


Figure 2
Top: the $R_2^2(8)$ motif in CBA, with O···O = 2.588 (3) Å, O—H = 0.997 (6) Å and H···O = 1.595 (6) Å. Bottom: the $R_2^2(7)$ motif in (I), with O···O = 2.5752 (14) Å, O—H = 0.92 (2) Å, (O)H···O = 1.66 (2) Å and (C—)H···O = 2.716 (14) Å.

Crystal data

$C_7H_5ClO_2{\cdot}C_3H_7NO$	D_x = 1.383 Mg m^{-3}
M_r = 229.66	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2512 reflections
a = 6.1269 (2) Å	θ = 1.0–27.5°
b = 14.6159 (5) Å	μ = 0.33 mm^{-1}
c = 12.6541 (4) Å	T = 123 (2) K
β = 103.228 (2)°	Cut fragment, colourless
V = 1103.11 (6) Å^3	0.50 × 0.45 × 0.40 mm
Z = 4	

Data collection

Nonius KappaCCD diffractometer	R_{int} = 0.033
φ and ω scans	θ_{max} = 27.5°
Absorption correction: none	$h = -7 \rightarrow 7$
10331 measured reflections	$k = -18 \rightarrow 18$
2488 independent reflections	$l = -16 \rightarrow 16$
2049 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2 + 0.445P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.035	
$wR(F^2)$ = 0.086	
S = 1.02	$(\Delta/\sigma)_{max} < 0.001$
2488 reflections	$\Delta\rho_{max}$ = 0.26 e Å^{-3}
146 parameters	$\Delta\rho_{min}$ = −0.31 e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

O1—C7	1.3257 (16)	O3—C8	1.2400 (16)
O2—C7	1.2149 (16)		
C6—C1—C2	119.67 (12)	C5—C6—C1	120.25 (12)
C3—C2—C1	120.76 (12)	O2—C7—O1	123.90 (12)
C2—C3—C4	118.25 (12)	O2—C7—C1	123.13 (12)
C5—C4—C3	122.26 (12)	O1—C7—C1	112.97 (11)
C4—C5—C6	118.81 (13)		

The H atoms involved in hydrogen bonding were located in a difference map and refined isotropically, but all other H atoms were constrained to idealized geometry with a riding model: for CH_3, $U_{iso}(H) = 1.5U_{eq}(C)$ and C—H = 0.98 Å; for CH, $U_{iso}(H) = 1.2U_{eq}(C)$ and C—H = 0.95 Å.

Data collection: *DENZO* (Hooft, 1988) and *COLLECT* (Otwinowski & Minor, 1997); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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supporting information

Acta Cryst. (2004). E**60**, o1950–o1951 [https://doi.org/10.1107/S1600536804024511]

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c = 12.6541 (4) Å
β = 103.228 (2)°
V = 1103.11 (6) Å^3
Z = 4
$F(000)$ = 480
D_x = 1.383 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2512 reflections
θ = 1.0–27.5°
μ = 0.33 mm^{-1}
T = 123 K
Cut fragment, colourless
0.50 × 0.45 × 0.40 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
10331 measured reflections
2488 independent reflections
2049 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 27.5°, θ_{min} = 2.2°
$h = -7 \rightarrow 7$
$k = -18 \rightarrow 18$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.086
S = 1.02
2488 reflections
146 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2 + 0.445P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.48550 (7)	0.33679 (3)	0.46220 (3)	0.04267 (14)
O1	0.75372 (17)	0.42666 (7)	−0.00788 (8)	0.0317 (2)
O2	1.03650 (16)	0.33076 (7)	0.06058 (8)	0.0292 (2)
O3	−0.08773 (16)	0.06015 (7)	0.32101 (8)	0.0294 (2)
N1	0.17573 (19)	0.10376 (8)	0.23148 (9)	0.0240 (2)
C1	0.7701 (2)	0.36572 (9)	0.16601 (10)	0.0223 (3)
C2	0.8882 (2)	0.31796 (9)	0.25654 (11)	0.0248 (3)
H2	1.0282	0.2907	0.2550	0.030*
C3	0.8037 (2)	0.30975 (10)	0.34867 (11)	0.0269 (3)
H3	0.8840	0.2773	0.4104	0.032*
C4	0.5986 (2)	0.35026 (10)	0.34838 (11)	0.0270 (3)
C5	0.4786 (2)	0.39844 (10)	0.26020 (11)	0.0264 (3)
H5	0.3392	0.4259	0.2623	0.032*
C6	0.5655 (2)	0.40599 (9)	0.16836 (11)	0.0248 (3)
H6	0.4849	0.4388	0.1069	0.030*
C7	0.8688 (2)	0.37198 (9)	0.06848 (11)	0.0239 (3)
C8	0.0964 (2)	0.09489 (9)	0.31984 (11)	0.0246 (3)
C9	0.0485 (3)	0.07220 (12)	0.12662 (11)	0.0370 (4)
H9A	−0.0924	0.0447	0.1350	0.056*
H9B	0.1362	0.0265	0.0976	0.056*
H9C	0.0159	0.1241	0.0764	0.056*
C10	0.3929 (2)	0.14543 (11)	0.23470 (13)	0.0340 (3)
H10A	0.4643	0.1620	0.3097	0.051*
H10B	0.3723	0.2005	0.1893	0.051*
H10C	0.4882	0.1018	0.2072	0.051*
H8	0.194 (2)	0.1190 (10)	0.3852 (12)	0.025 (4)*
H1	0.823 (4)	0.4279 (15)	−0.0653 (18)	0.066 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0402 (2)	0.0637 (3)	0.02799 (19)	−0.00013 (19)	0.01599 (16)	0.00366 (18)
O1	0.0328 (5)	0.0397 (6)	0.0245 (5)	0.0101 (5)	0.0107 (4)	0.0074 (4)
O2	0.0267 (5)	0.0339 (6)	0.0279 (5)	0.0057 (4)	0.0082 (4)	−0.0019 (4)
O3	0.0279 (5)	0.0350 (6)	0.0273 (5)	−0.0034 (4)	0.0102 (4)	−0.0029 (4)
N1	0.0243 (6)	0.0241 (6)	0.0235 (5)	0.0002 (5)	0.0053 (4)	−0.0004 (5)
C1	0.0235 (6)	0.0198 (6)	0.0238 (6)	−0.0014 (5)	0.0053 (5)	−0.0014 (5)
C2	0.0238 (7)	0.0232 (7)	0.0266 (7)	0.0017 (5)	0.0042 (5)	−0.0005 (5)
C3	0.0292 (7)	0.0266 (7)	0.0236 (6)	−0.0009 (6)	0.0035 (5)	0.0026 (5)
C4	0.0287 (7)	0.0303 (8)	0.0231 (6)	−0.0064 (6)	0.0085 (5)	−0.0036 (6)

C5	0.0239 (7)	0.0264 (7)	0.0299 (7)	0.0006 (6)	0.0082 (5)	−0.0017 (6)
C6	0.0248 (7)	0.0230 (7)	0.0257 (6)	0.0004 (5)	0.0039 (5)	0.0019 (5)
C7	0.0238 (6)	0.0239 (7)	0.0233 (6)	−0.0011 (5)	0.0036 (5)	−0.0018 (5)
C8	0.0275 (7)	0.0228 (7)	0.0228 (6)	0.0003 (5)	0.0043 (5)	−0.0011 (5)
C9	0.0358 (8)	0.0513 (10)	0.0234 (7)	−0.0045 (7)	0.0056 (6)	−0.0031 (7)
C10	0.0303 (7)	0.0355 (9)	0.0380 (8)	−0.0060 (6)	0.0114 (6)	0.0000 (7)

Geometric parameters (Å, º)

Cl1—C4	1.7463 (14)	C3—H3	0.950
O1—C7	1.3257 (16)	C4—C3	1.389 (2)
O1—H1	0.92 (2)	C4—C5	1.380 (2)
O2—C7	1.2149 (16)	C5—H5	0.950
O3—C8	1.2400 (16)	C6—C5	1.3889 (18)
N1—C8	1.3238 (17)	C6—H6	0.950
N1—C9	1.4518 (17)	C8—H8	0.969 (15)
N1—C10	1.4552 (18)	C9—H9A	0.980
C1—C6	1.3915 (18)	C9—H9B	0.980
C1—C7	1.4963 (18)	C9—H9C	0.980
C2—C1	1.3942 (18)	C10—H10A	0.980
C2—H2	0.950	C10—H10B	0.980
C3—C2	1.3848 (19)	C10—H10C	0.980
C7—O1—H1	108.8 (13)	C5—C6—H6	119.9
C8—N1—C9	121.11 (12)	C1—C6—H6	119.9
C8—N1—C10	121.84 (12)	O2—C7—O1	123.90 (12)
C9—N1—C10	117.05 (11)	O2—C7—C1	123.13 (12)
C6—C1—C2	119.67 (12)	O1—C7—C1	112.97 (11)
C6—C1—C7	121.86 (12)	O3—C8—N1	124.14 (12)
C2—C1—C7	118.47 (12)	O3—C8—H8	121.6 (9)
C3—C2—C1	120.76 (12)	N1—C8—H8	114.3 (9)
C3—C2—H2	119.6	N1—C9—H9A	109.5
C1—C2—H2	119.6	N1—C9—H9B	109.5
C2—C3—C4	118.25 (12)	H9A—C9—H9B	109.5
C2—C3—H3	120.9	N1—C9—H9C	109.5
C4—C3—H3	120.9	H9A—C9—H9C	109.5
C5—C4—C3	122.26 (12)	H9B—C9—H9C	109.5
C5—C4—Cl1	119.07 (11)	N1—C10—H10A	109.5
C3—C4—Cl1	118.64 (11)	N1—C10—H10B	109.5
C4—C5—C6	118.81 (13)	H10A—C10—H10B	109.5
C4—C5—H5	120.6	N1—C10—H10C	109.5
C6—C5—H5	120.6	H10A—C10—H10C	109.5
C5—C6—C1	120.25 (12)	H10B—C10—H10C	109.5
C7—C1—C6—C5	179.74 (13)	C4—C3—C2—C1	0.0 (2)
C2—C1—C6—C5	−0.2 (2)	C5—C4—C3—C2	−0.4 (2)
C2—C1—C7—O1	−173.46 (12)	Cl1—C4—C3—C2	177.67 (11)
C2—C1—C7—O2	6.8 (2)	Cl1—C4—C5—C6	−177.60 (11)

C6—C1—C7—O1	6.56 (18)	C3—C4—C5—C6	0.5 (2)
C6—C1—C7—O2	−173.18 (13)	C1—C6—C5—C4	−0.2 (2)
C3—C2—C1—C6	0.3 (2)	C9—N1—C8—O3	−0.1 (2)
C3—C2—C1—C7	−179.68 (12)	C10—N1—C8—O3	179.77 (13)